Self-ignition in stone wool insulation contaminated with fatty acid (fundamentals, case study, analysis methodology)

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ABSTRACT

A combination of a residual film of flammable organic substance, air and porous structures like insulation material (e.g. stone wool) may result in a fire. The initiating self-heating process depends on the substance (reactivity, volatility), amount of accumulated liquid, volume and temperature. Specific information is given for application and extension of the Thomas criterion with a 2nd order reaction. The experimental part includes new experimental techniques to determine heat transfer and formal reaction kinetic data. The applied self-ignition temperature (SIT) simulation model relies on liquid film volume and not on liquid film surface reaction. As a further result of the studies detailed working procedure of three simplified methodologies for estimation of SITs in technical scale are presented. New techniques to determine parameters necessary for SIT prediction, especially in combination with Methodology III, have the power to reduce the costs for estimating the SIT up to 80%.

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1. Introduction

Organic liquid in contact with insulation material has already often resulted in lagging fires (Gugan, 1974; Brindley, 1998b; Lees, 2005) and sometimes as a consequence of this, in an explosion (Mellin, 1991). Self-heating in insulation materials has been studied over several decades. In the last two decades, extension of analysis of these phenomena has been centred on fundamental theoretical studies (Bowes, 1974; Buch, 1985; Britton, 1991; Brindley, 1999). The outcome of these studies does not include proposals for effective determination of SIT under practical constraints and effective determination of simulation parameters. The motivation of this study is to close that gap.

In order to solve that target, new techniques for determination of heat transport and reaction kinetic parameters based on equipment already used for SIT experiments have been developed. Based on two dynamic laboratory experiments, specific data analysis and simulation of the self-heating process determination of SITs for technical sizes is presented. The power of the methodologies developed is: definition of the procedures (experimental constraints, analysis of 2nd order reaction kinetics) and reduction of

analysis time. Another focus of this study is related to demonstration of the power of simulation for SIT studies. Finally, study results document that the reaction kinetic is depending on conversion and that the reaction takes place in the liquid film and not at the surface.

1.1. Theoretical fundamentals

The well known methods for determination of self-ignition temperature (SIT) of dusts (Frank-Kamenetskii, 1959; Thomas, 1960) - based on the heat balance only - have already been extended for determining the self-ignition of insulation that has been contaminated with organic liquids. In addition to the overall heat balance, it is necessary to consider the consumption and loss of organic liquid (raw material), transport of organic vapour (raw material) and transport and consumption of oxygen (Brindley, 1998a, 1998b). Convective terms are discussed but - because of large pressure drop - not included in the balances (Brindley, 1998a).

All simulation and experimental results are based on open systems. However, in most instances commonly found in technical practice, the insulation is surrounded by an outer shell. Loss of organics is therefore assumed to be reduced. As a consequence of this, the self-ignition temperatures developed for open systems may not be conservative for installed insulation contaminated with organic liquid.

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There are two criteria used for the differentiation between self-heating and self-ignition.

Temperature criterion (criterion A)

The standard criterion for determining of self-ignition of dusts or self-ignition in insulation (Britton, 1991) is based on a predefined temperature level, which must be reached in the centre of the sample. According to the German VDI-standard used for dusts (VDI 2263, 1990) this temperature level should exceed a temperature of 400 °C. In the UN Recommendations on the Transport of Dangerous Goods (2009) a much lower temperature level (200 °C) is used for the classification into Division 4.2, Spontaneous combustible substances. Criterion data used in this study:

No ignition: temperature in the centre of the sample is < 400 °C.
Ignition: temperature in the centre of the sample is > 400 °C.
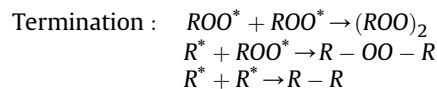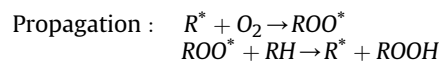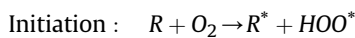
Temperature difference criterion (criterion B)

This criterion is based on the temperature difference observed between the centre of the sample and the oven. If that temperature difference is greater than the predefined level, of, for example 50 °C, it is assumed that modified test conditions may initiate further reaction steps with the consequence of fire. This criterion has - in addition to the standard criterion - already been used by other researchers (e.g. Britton, 1991; Brindley, 1999). In the UN Recommendations on the Transport of Dangerous Goods (2009) a temperature difference of 60 °C is used for the classification into Division 4.2. Criterion data used in this study:

No ignition: temperature difference between centre of sample and oven is < 50 °C.
Ignition: temperature difference between centre of sample and oven is > 50 °C.

Lipid autoxidation

Different mechanisms of first steps of the autoxidation have been published. The principles are described in detail in literature (Litwinienko, 2005; Kamal-Eldin, 2005). The autoxidation can be divided into the following steps:

$$\text{Initiation}: \quad R + O_2 \rightarrow R^* + HOO^*$$

$$\text{Propagation}: \quad \begin{aligned} R^* + O_2 &\rightarrow ROO^* \\ ROO^* + RH &\rightarrow R^* + ROOH \end{aligned}$$

$$\text{Termination}: \quad \begin{aligned} ROO^* + ROO^* &\rightarrow (ROO)_2 \\ R^* + ROO^* &\rightarrow R-OO-R \\ R^* + R^* &\rightarrow R-R \end{aligned}$$

2. Theoretical basis

2.1. Determination of heat transfer data $(\lambda_\Sigma, \dot{h}_\Sigma^G)$

In case of zero-order reaction, no evaporation and no convection the self-ignition process can be described using the heat balance only (equation (1)).

$$\overline{\rho}_\Sigma \cdot \overline{c}_{p,\Sigma} \cdot \frac{\partial T}{\partial t} = \text{div}(\dot{\lambda}_\Sigma \cdot \nabla T) + \overline{\dot{q}}_{V,R}^L \tag{1}$$

Because of the porous structure of the system not all of the parameters (heat transfer data and kinetic data) are known or can be calculated. Therefore, techniques used to determine heat transfer and reaction data are presented first.

If the reaction can be neglected (inert gas, low temperature) equation (1) can be simplified to equation (2).

$$\overline{\rho}_\Sigma \cdot \overline{c}_{p,\Sigma} \cdot \frac{\partial T}{\partial t} = \text{div}(\dot{\lambda}_\Sigma \cdot \nabla T) \tag{2}$$

Initial condition:

$T = T_{ambient}$ for all r and z

Boundary conditions:

$$\text{Surface}: \quad \pm\dot{\lambda}_\Sigma \cdot \frac{\partial T}{\partial r} = \dot{h}_{\Sigma, vertical}^G \cdot \left(T_{surface} - T_{ambient} \right) \quad \text{for } r = \pm r_0 \tag{3}$$

$$\text{Surface}: \quad \pm\dot{\lambda}_\Sigma \cdot \frac{\partial T}{\partial z} = \dot{h}_{\Sigma, horizontal}^G \cdot \left(T_{surface} - T_{ambient} \right) \quad \text{for } z = \pm z_0/2 \tag{4}$$

$$\text{Core}: \quad \frac{\partial T}{\partial r} = 0 \ \text{ for } r = 0 \quad \frac{\partial T}{\partial z} = 0 \ \text{ for } z = 0$$

The overall heat transfer coefficient $\dot{h}_{\Sigma,i}^G$ includes both heat transfer because of convection and heat radiation. The data depend on temperature, temperature difference and size of the sample.

For determination of heat transfer coefficient and heat conductivity the oven, surface and core temperature profiles of the sample during a heat-up experiment have to be measured and analysed. The standard start temperature is ambient temperature. The heating-up phase to the target temperature results in a dynamic change of the temperature difference between oven and sample temperature. The temperature difference between oven and surface temperature is an indication for the overall heat transfer coefficient and the temperature difference between surface and core temperature for the heat conductivity. For the simulation of surface and centre temperature profiles a computer program was developed. The program solves the equations for unsteady heat conduction using the finite difference method from Crank-Nicolson (Crank and Nicolson, 1947). Determination of heat transfer data is based on comparison of experimental and simulated temperature profiles at surface and centre of the sample. If the deviation between experimental and simulated temperature profiles is at minimum, then heat transfer data and/or correlation used in simulation are assumed as best estimate.

For heat conductivity

The comparison of temperature profiles at the core of the sample is used as a basis for the determination of the heat conductivity. If the heat conductivity of the porous structure does not depend very much on the temperature, a fixed representative value can be found for λ_Σ at test conditions. But, if an extended temperature range is used in the test $\lambda_\Sigma = f(T)$ has to be determined.

Remark: The heat conductivity of the porous structure depends on volume fraction of the liquid ($\varepsilon_{FA,0}^L$) and as well on volume fraction of stone wool ($\varepsilon_{stone\ wool}^S$).

For heat transfer coefficient

The comparison of temperature profiles at surface of the sample is used as the basis for validation or modification of the heat transfer correlation. Heat transfer at surface does include both convection and radiation effects. Heat transfer due to convection depends on surface position (horizontal, vertical). Convection and radiation effects can be considered by an overall heat transfer coefficient.